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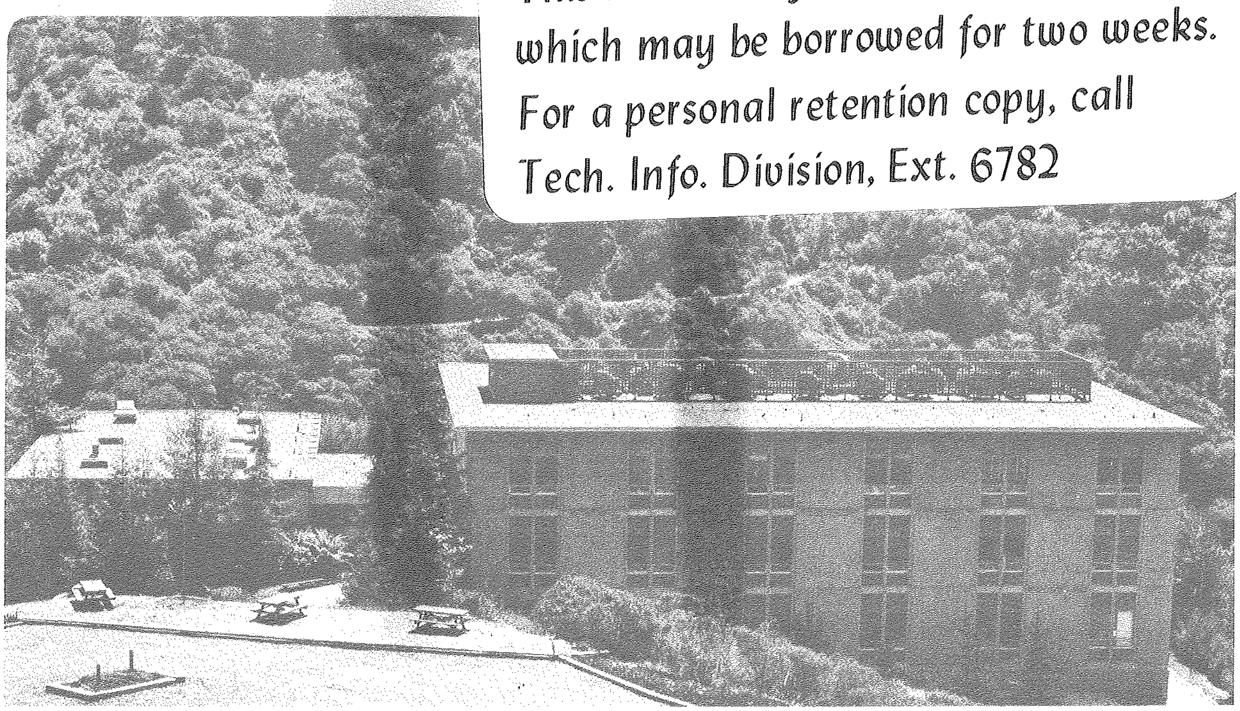

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EXACT SOLUTION (WITHIN A DOUBLE ZETA BASIS SET) OF SCHRÖDINGER'S ELECTRONIC EQUATION FOR WATER

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Abstract

Using recently developed theoretical techniques, it has been possible to achieve an exact variational solution of Schrödinger's Equation within a modest basis set of one-electron functions. The full configuration interaction for this system included a total of 256,473 $^1A_1$ spin-and space-adapted configurations. Comparison with many-body perturbation theory proves to be quite interesting.

Over the past decade, a relatively "standard" treatment of electron correlation in small molecules has evolved.[1,2] This standard treatment is applicable to systems for which the restricted Hartree-Fock method provides a qualitatively reasonable description of the electronic structure. In such cases, one is justified in employing configuration interaction (CI) including all configurations differing by one or two electrons from the Hartree-Fock reference configuration. For predictions of most properties of chemical interest, this CISD (CI including single and double excitations) procedure is a well-defined and sensible starting point for the description of electron correlation effects.[3] However, it seems equally clear that a key theoretical question to be addressed during the next decade is that of just how important are those higher order correlation effects[2] (or many-body effects, with the understanding that "many" means three or higher) ignored in CISD.

The importance of many-body correlation effects may be investigated by perturbation[4] or variational[1-3] methods, with the former often thought to be the more efficacious in this particular regard.[5] However, there are situations in which variational approaches can be uniquely helpful. The present research is a modest example of such a situation, in that an exact variational solution of Schrödinger's equation has been achieved, within a limited basis set, for the water molecule. This exact solution provides a benchmark by which the validity of less complete theoretical treatments may be judged.

Since the energy differences of interest here are in some cases quite small, it is exceedingly important (for future comparisons to be meaningful) that the exact technical details of the present work be laid out explicitly. The water basis set used here was of the standard contracted gaussian, double zeta variety. Specifically, Dunning's contraction[6a] of Huzinaga's primitive O(9s5p), H(4s) basis[7] was chosen. For hydrogen, a scale factor of $\zeta = 1.2$ was applied to the basis functions.[6b] The geometry used for the water molecule was precisely that of Laidig, Saxe, and Schaefer[8] and may be specified by the cartesian coordinates (in atomic units) of the three atoms: O(0.0, 0.0, -0.009), H_a(1.515 263, 0.0, - 1.058 898), H_b(-1.515 263, 0.0, -1.058 898). With this particular basis set and geometry, the single-configurations self-consistent-field (SCF) energy for water is -76.009 837 60 hartrees. For future comparisons with the present results to be significant, a minimum requirement is that the SCF energy be reproduced to all ten significant figures. This should guarantee that no confustion exists concerning the specification of the basis set and geometry. Although the present research was carried out on the CDC 7600 (60 bit word length), it was possible to reproduce the SCF energy to better than nine significant figures on the 48 bit Harris Series 800 minicomputer.

The Hartree-Fock reference configuration for H_2O is of the general form

$$1a_1^2 \ 2a_1^2 \ 1b_2^2 \ 3a_1^2 \ 1b_1^2 \qquad (1)$$

With the standard double zeta basis there are 19 single excitations, 341 double excitations, 2,842 triple excitations, and 14,475 quadruple excitations. CI studies up to the S + D + T + Q level have been previously carried out[8] via the unitary group approach,[9,10] and are reproduced in the Table. As noted earlier, the purpose of the present paper is to report a full CI for double zeta water. To our knowledge the only previous variational studies of higher than quadruple excitations are those of Shavitt and co-workers.[11]

For the present water example, there are 41,952 quintuple excitations, 72,365 sextuple excitations, 71,434 seven-fold excitations, 40,046 eight-fold excitations, 11,492 nine-fold excitations, and 1506 ten-fold excitations. Thus the full CI includes a total of 256,473 $^1A_1$ spin- and space-adapted configurations.

This very large CI was made possible by the recently developed integer-based algorithm due to Handy.[12] All one- and two-electron integrals were kept to full 14 significant figure floating point accuracy, while the CI coefficients were stored as 24-bit integers, allowing more than six significant figures of precision. This and the five iterations used during the diagonalization step should ensure an absolute accuracy of 10^{-6} hartree for the full CI energy. The new program was tested for a ten molecular orbital full CI by using various unitary transformations amongst the orbitals and noting that the total energy was unchanged.

The Table compares the results of the present full CI with previous variational results for the same system and with the many-body perturbation study of Bartlett.[13] The exact correlation energy for this model system is -0.148 028 hartrees, the difference between the full CI and SCF energies. Given this result one can state precisely that single and double excitations account for 94.7% of the correlation energy and that triple and quadruple excitations amount to 5.13%. All higher excitations (that is to say 238,795 of the 256,473 total configurations) lower the CIS+D+T+Q **total energy** by only 0.000 263 hartrees, or 0.18% of the total correlation energy. This is a very encouraging result in that it confirms one's intuitive feeling[2,3] that these higher-order correlation effects are relatively unimportant for 10 electron molecules such as water.

Comparison with the MBPT results of Bartlett, Wilson, and Guest[13,14] is also of considerable interest. Their fourth-order treatment includes 99.33% of the correlation energy, implying an error just about three times that found for the CIS+D+T+Q variational result. The difference between the second-order perturbation energy and the exact energy is 0.008 550 hartrees, or 5.8% of the correlation energy. The remaining correlation energy picked up by MBPT is 0.007 561 hartrees. This means that the fourth-order procedure accounts for 756/855 or 88.4% of the correlation energy obtainable from third through infinite order perturbation theory.

Two-thirds of the remaining 11.6% of the correlation energy due to third through infinite orders may be accounted for by the coupled cluster doubles (CCD) model, which involves an infinite-order sum of double -and ("disconnected") quadruple- excitation effects.[15] Bartlett's unpublished results[13] allow us to examine the importance of these higher-order correlation effects. Comparison between CCD (-0.145435 hartrees) and the double and quadruple excitation MBPT energy through fourth order (-0.144767) yields -0.000668 hartrees for the difference. This difference amounts to 7.8% of the correlation energy beyond second order, leaving only 3.8% unaccountable for in the *ab initio* sense. Since this level of MBPT accounts for 99.78% of the total correlation energy, it can be concluded that the agreement between variation and perturbation methods is quite satisfactory.

Acknowledgement

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Table. Comparison between exact results for double zeta H_2O and approximate results obtained via variational and perturbation techniques.

Variational Results

Wave Function	Number of Configurations	Total Energy	Correlation Energy	Energy Relative to CI S+D	Coefficient C_0 of Reference Configuration
Self-Consistent-Field (SCF)	1	-76.009 838	0.0	--	1.0
CI All Double Excitations (D)	342	-76.149 178	-0.139 340	+0.000 837	0.979 38
CI All Single and Double Excitations (S+D)	361	-76.150 015	-0.140 177	0.C	0.978 74
CI All S + D + T	3,203	-76.151 156	-0.141 318	-0.001 141	0.978 19
CI All D + Q	14,817	-76.155 697	-0.145 859	-0.005 682	0.976 68
CI All S + D + T + Q	17,678	-76.157 603	-0.147 765	-0.007 588	0.975 43
Full CI	256,473	-76.157 866	-0.148 028	-0.007 851	0.975 28

Many-Body Perturbation Theory (Bartlett)[a]

	Correlation Contribution	Commulative Correlation Energy	Energy Relative to CI S + D
Second-Order Energy	-0.139478	-0.139478	+0.000699
Third-Order Energy	-0.001391	-0.140869	-0.000692
Fourth-Order			
Linked Diagram Double Excitations	-0.003083	-0.143952	-0.003775
Linked Diagram Single Excitations	-0.000908	-0.144860	-0.004683
Linked Diagram Quadruple Excitations	-0.000815	-0.145675	-0.005498
Linked Diagram Triple Excitations [b]	-0.001364	-0.147039	-0.006862
Coupled Clusted Doubles (CCD)		-0.145435	-0.005258
CCD + Fourth-Order Singles and Triples		-0.147707	-0.007530

[a] R. J. Bartlett, private communication. See also Reference 4.

[b] Reference 14.